Separation of CO_2 from Flue Gases by Carbon – Multiwall Carbon Nanotube Membranes

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Abstract

The feasibility of using a novel carbon-multiwall carbon nanotube membrane for separating CO_2 from the flue gas effluent of power generation plant is being studied. Such an innovative membrane system offers many unique advantages over existing technologies: refractory carbon-carbon membranes are resistant to temperature and chemical attack, the multiwall nanotube derived pores in the membrane are mono-disperse, the pore size can be controlled, and the rapid kinetic and diffusion rates will yield high permeate fluxes. As the first step toward design and construction of a working carbon-carbon nanotube based membrane, specific goals have included evaluation of the separation mechanism, either diffusive or adsorptive, and a test to demonstrate proof-of-concept separation. Experimental work has determined uptakes and separation efficiencies for CO_2 and N_2 mixtures by open ended multiwall carbon nanotubes.

As-produced multiwall nanotubes are open at one end, but contain small particulate inclusions of iron catalyst blocking access to the core. We have found that a simple graphitization step (heating to 1800 ?C in an inert atmosphere) removes this iron contaminant, greatly enhancing adsorption within the nanotube core. We have produced and graphitized 10 grams of MWNT, allowing for bench scale studies on these materials. Static adsorption isotherms for both N_2 and CO_2 have been measured on MWNTs. The MWNTs show little uptake of N_2 over the pressure range 0.5 to 5 bar. In contrast, the measured uptake of CO_2 on MWNT at 30 ?C was found to be two orders of magnitude greater than for N_2 over the same pressure range. The MWNTs exhibit significant CO_2 adsorption capacities over this pressure range for operating temperatures in excess of 150 ?C.

A fixed bed containing 0.25g of the graphitized multiwall nanotubes was tested for its ability to separate CO_2 from N_2 from a gas flow of 100 SCCM containing equal quantities of the two components. Prior to

breakthrough, CO_2 was retained for 0.4 min, illustrating the efficacy of these materials for separating the two gases. Further refinement of the bed separations at higher temperatures and pressures is being pursued, as is the formation of single-layer nanotube membranes.

Computational modeling has been used to assess the interaction between various gas molecules and the carbon nanotubes. In this study, classical molecular dynamics simulations are used to investigate the diffusive flow of pure molecules and binary molecular mixtures through carbon nanotubes. Standard Lennard-Jones potentials are used to model the intermolecular interactions. Both H-terminated and C-terminated open nanotube ends have been considered. The specific molecules and binary systems that are being examined include methane, ethane, nitrogen, oxygen, carbon dioxide, methane/ethane, methane/n-butane, methane/isobutane, nitrogen/oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide. The simulations predict which binary mixtures separate as a result of this diffusive flow and which remain mixed. They also indicate how these results depend on the nanotube properties such as core diameter and helical symmetry. The simulations provide information about how the structure and size of the molecules in the mixtures influence the results. For example, n-butane and isobutane are predicted to have significantly different separation behaviors when they are mixed with methane molecules. In addition, molecules with non-spherical aspect ratios exhibit different behavior than spherical molecules that affects both their diffusion mechanisms and their separation in mixtures. The study includes individual nanotubes and nanotubes in bundles and the degree of separation predicted depends on whether the nanotubes are retained as cohesive bundles.